# Microbial Induced Degradation of Cement-Solidified Waste Forms For Radioactive Waste Disposal

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# Presentation Outline

- Introduction
  - Cement solidification and stabilization waste forms.
  - U.S. Nuclear Regulatory Commission's microbial stability test protocol for radioactive solidification waste forms.
- Project Objectives
- Experimental Approach
- Results and Discussions
- Conclusions

# Introduction

- The goal of solidification & stabilization (s/s), as a radioactive waste disposal technique, is to encapsulate the waste in a stable solid matrix (waste form) for safe long-term disposal (e.g. Yucca Mountain Repository Project).

- The U.S. Nuclear Regulatory Commission (NRC) require long term stability performance tests on all waste forms before disposal.

# Introduction (contd.)

- Microbial induced degradation (MID) is a major problem area in long-term stability of all solidification waste forms.
- NRC Regulation 10 CFR 61.56(b)(1) requires evaluation of physical, chemical, & **microbial stability** of waste forms for classes B and C low level radioactive wastes.

# Introduction (contd.)

- The NRC established a **microbial stability test protocol** involving the use of sulfur oxidizing bacteria (SOB), e.g. *Thiobacillus thiooxidans (T.t),* as the test microbes.

- Since its inception in 1987, the NRC **microbial stability test protocol** has been controversial due to several technical limitations.

# Introduction (contd.)

- One major area of controversy is the NRC test protocol's inability to account for the effects of the test media acidity (pH) on the test sample stability.

- This project was designed to address some of the technical inadequacies of the NRC's microbial stability test protocol for cement-solidified waste forms.

# Project Objectives

- To conduct an experimental evaluation of the NRC's microbial stability protocol with a view to identifying the technical limitations, if any.

- Develop an alternative test protocol to address identified technical limitations.

# Experimental Approach

- **Microbial culture:**
  - **The sulfur oxidizing bacteria (SOB) *Thiobacillus thiooxidans (T.t),* an aerobic chemoautotroph, was supplied by INEEL and used for the study.**
  - **The microbial growth medium consisted of (g/L):**
    - **$MgSO_4.6H_20$ (0.4)**
    - **$(NH4)_2SO_4$ (0.5),**
    - **$K_2S_4O_6$ (3.0) – potassium tetrathionate (main source of sulfur)**
    - **$KH_2PO_4$ (3.0)**
    - **$CaCl_2$ (0.1), and $FeSO_4$ (0.01)**
  - **A New Brunswick (Bioflow III) Bioreactor was used to grow the microorganism.**

# Experimental Approach (contd.)

# Experimental Approach (contd.)

- *Thiobacillus thiooxidans (T.t)* derives metabolic energy from the oxidation of sulfur compounds, such as $H_2S$ and Potassium Tetrathionate:

$$2K_2S_4O_6 + 6H_2O + 7\ O_2$$

$$\downarrow\ T.t$$

$$2K_2SO_4\ +\ 6H_2SO_4$$

# Experimental Approach (contd.)

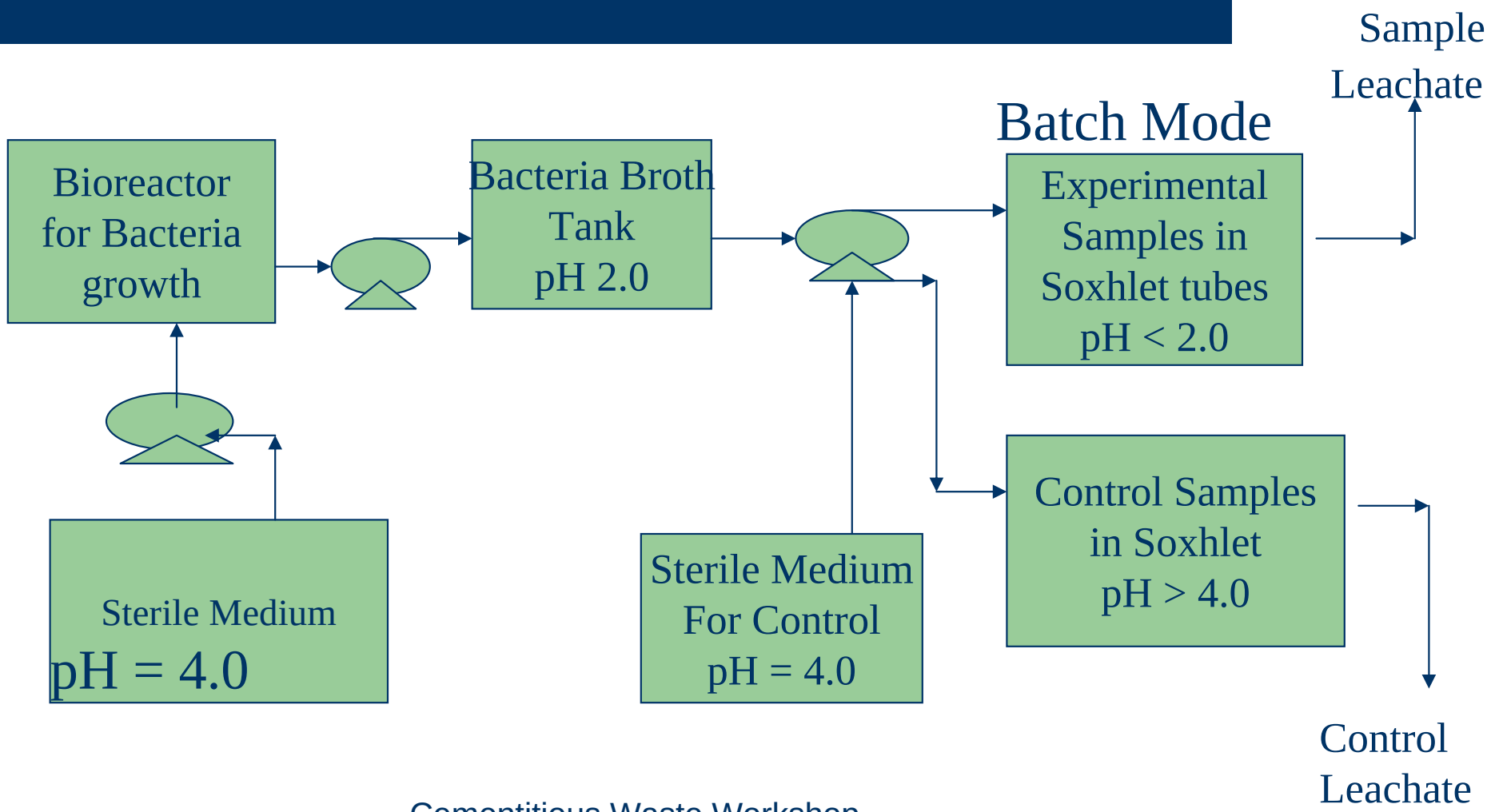
- Cement-Solidified Waste Form Samples:
  - **Prepared from Portland Type 1 cement, as 2.0 parts cement to 1.0 part water.**
  - **For some samples, cobalt chloride (21 wt%) was added to the cement mixture to simulate radioactive wastes before allowing to set in plastic moulds for 28 days.**
  - **Final samples consisted of cylindrical cement-solidified waste-forms measuring 2.0 cm in height and 1.5 cm in diameter.**

# Experimental Approach (contd.)

- **Chemical Analysis**:
  - **Waste form degradation was assessed by measuring the amounts of metallic constituents (Ca, Mg, & Co), released in leachates during testing.**
  - **Metallic constituents in leachates and fermenter broths were determined by Perkin Elmer ICP Spectrophotometer (model 3300 DV Optima).**
  - **Sulfate concentrations in media and leachates were determined by UV absorbance at 420 nm after $BaCl_2$ precipitation, using a spectrophotometer.**

# Experimental Setup (Soxhlet extraction system)

# Flow Diagram of NRC Test Protocol

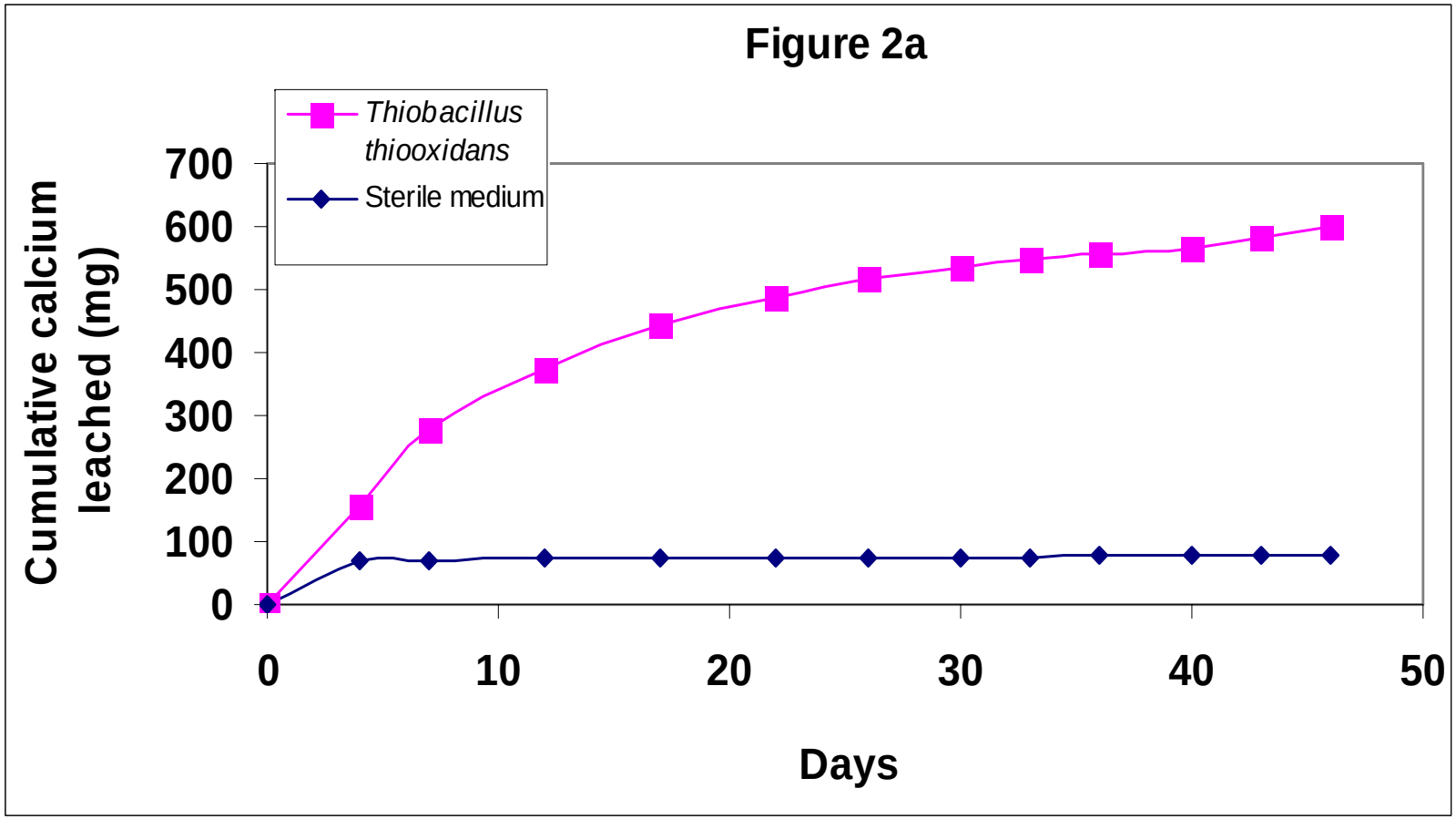


# Results and Discussion

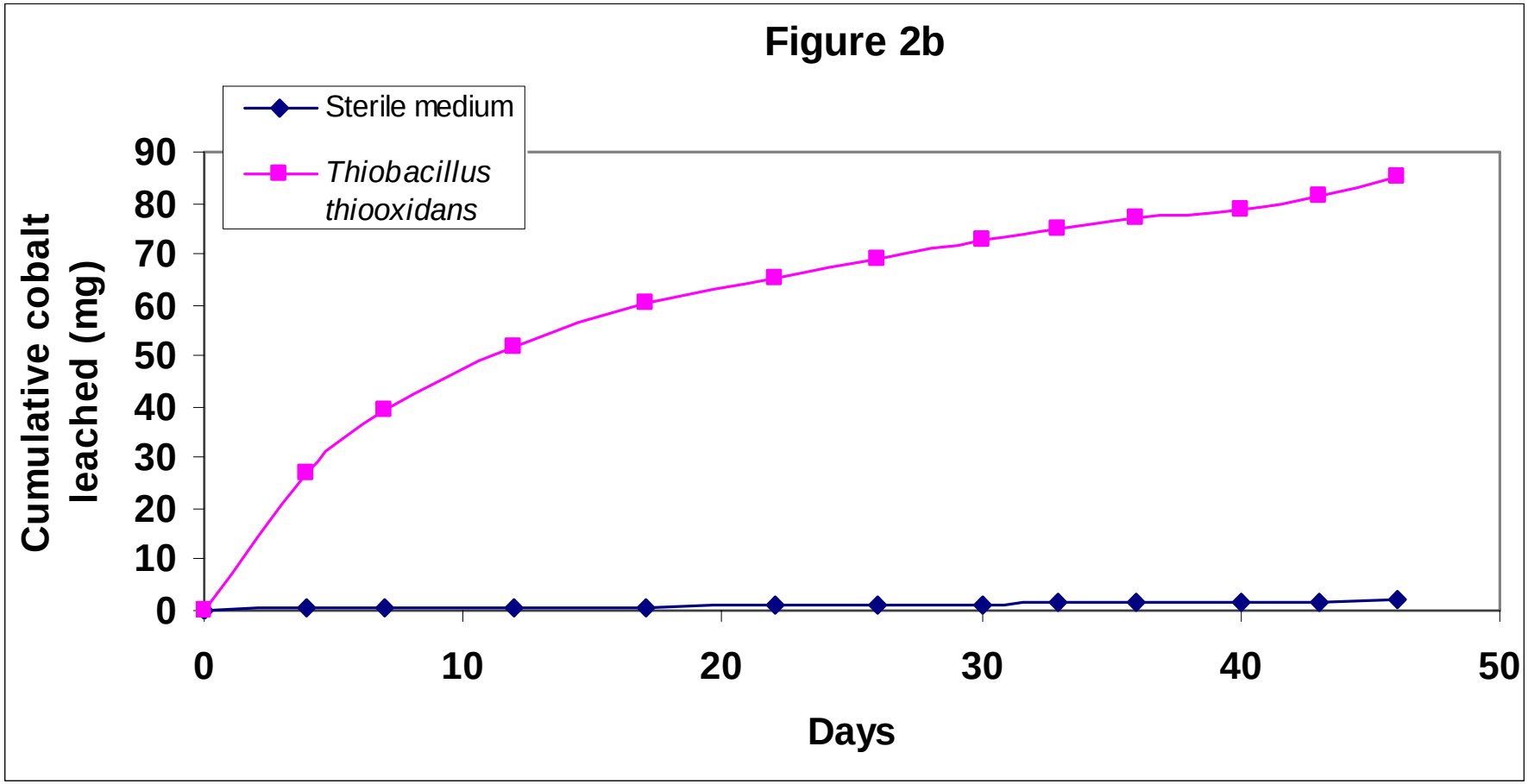
- Composition of Cement-Solidified Waste Form Samples (21 wt.% cobalt chloride):
  - Calcium ~ 5,580 mg
  - Cobalt ~ 1,840 mg (3,990 mg as $CoCl_2$)
  - Magnesium ~ 380 mg

- 100% Cement waste Form
  - Calcium ~ 8,900 mg
  - Magnesium ~ 640 mg

# Effect of *T.t* on the leaching of calcium from cement/cobalt waste form using the NRC method (21 wt.% cobalt chloride)

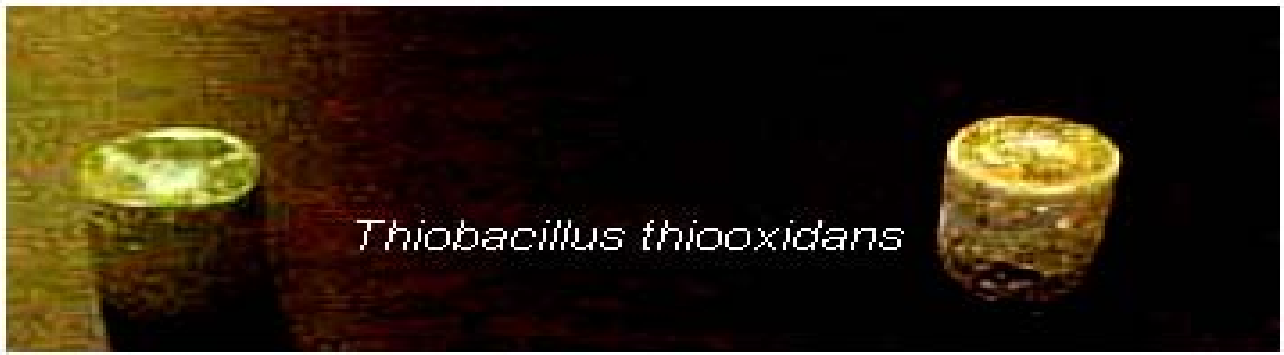


# Effect of *T.t* on the leaching of Cobalt from cement/cobalt waste form using the NRC method (21 wt.% cobalt chloride)

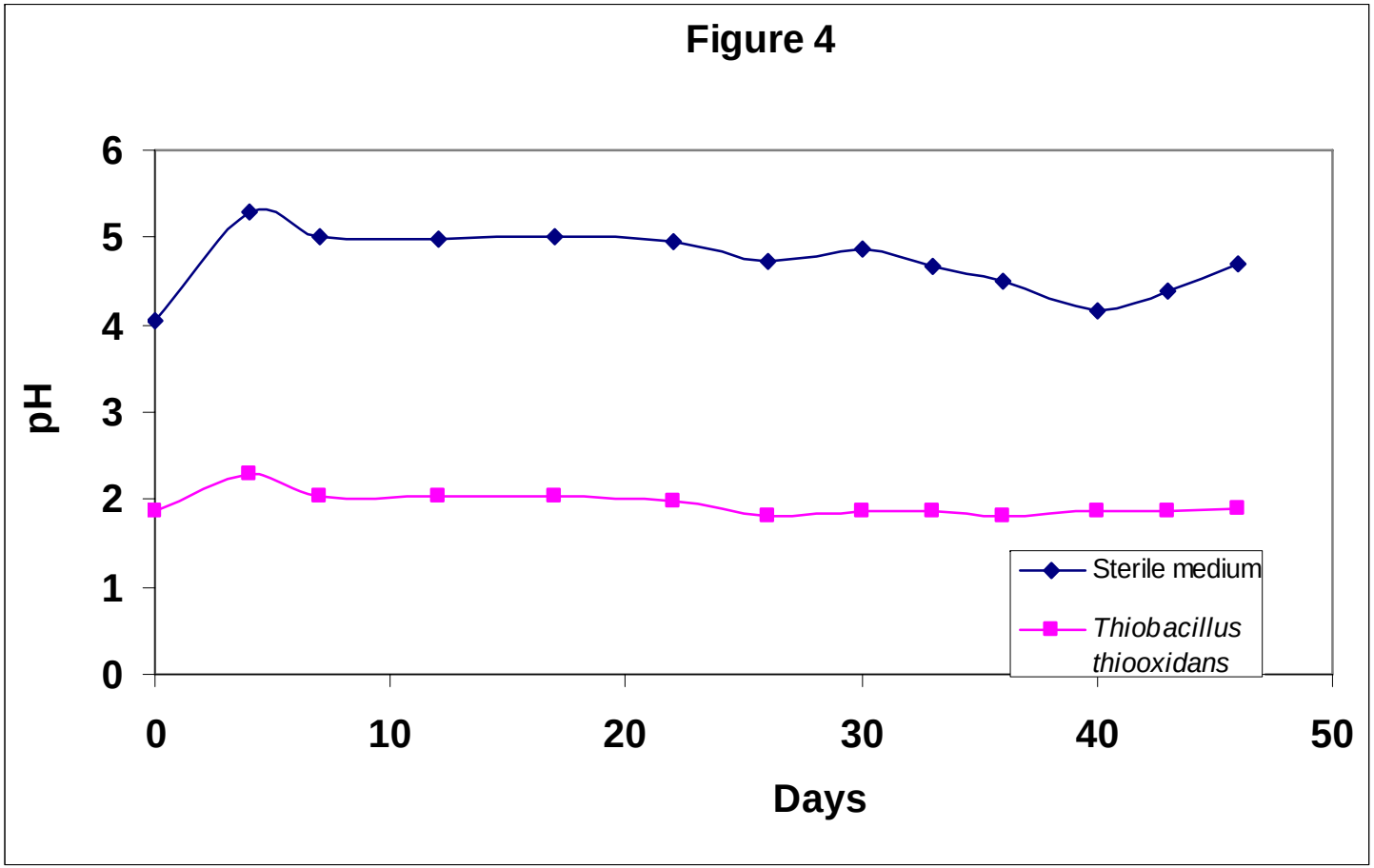


# Physical deterioration of cement/cobalt waste form with exposure to *T.thiooxidans*

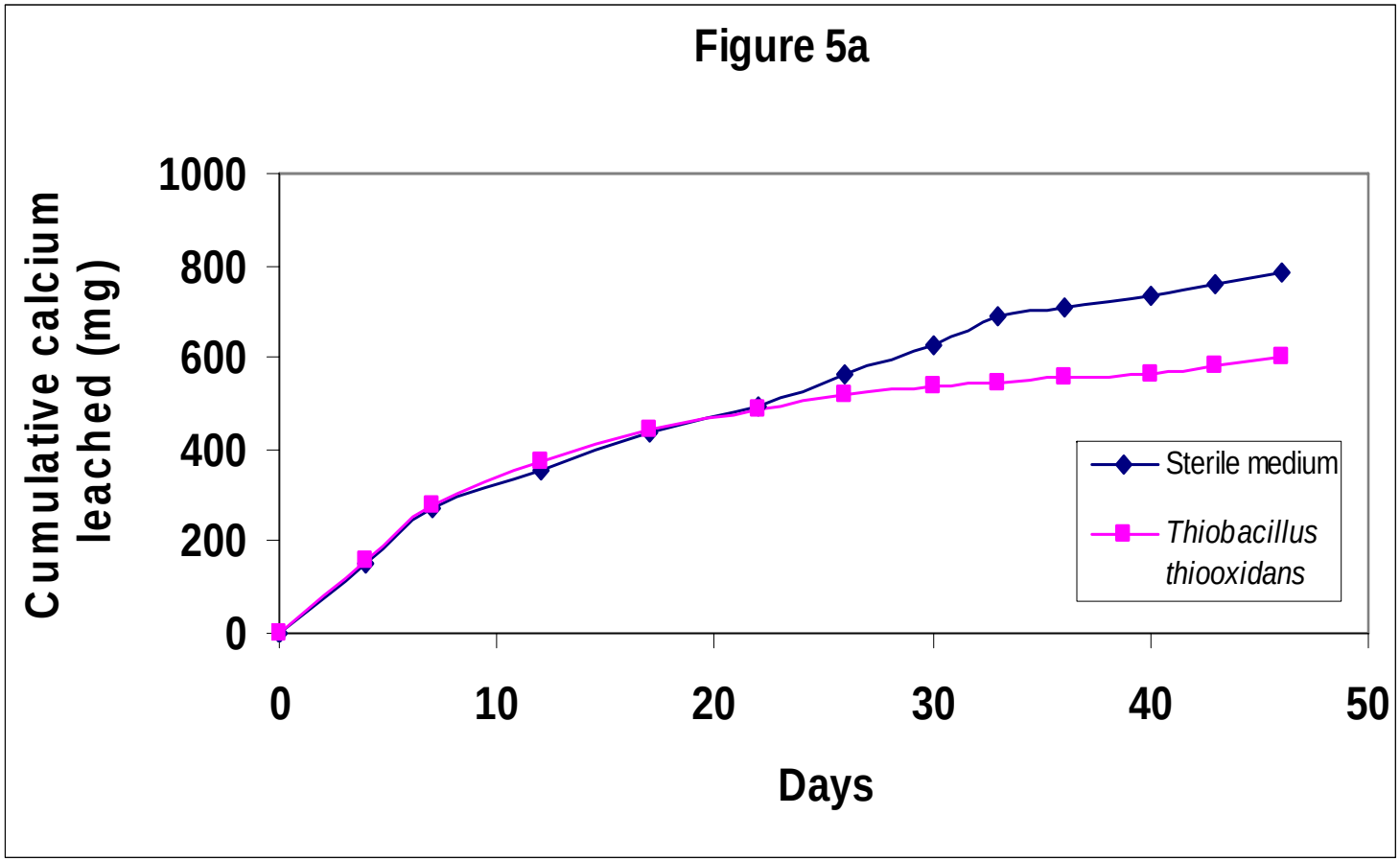

**Before exposure** **After exposure**



# pH of lixiviants vs. exposure time for cement/cobalt waste forms



# Calcium leached on exposure of waste forms to *Bacteria* and sterile medium at similar pH using NRC test protocol (pH = 1.9).



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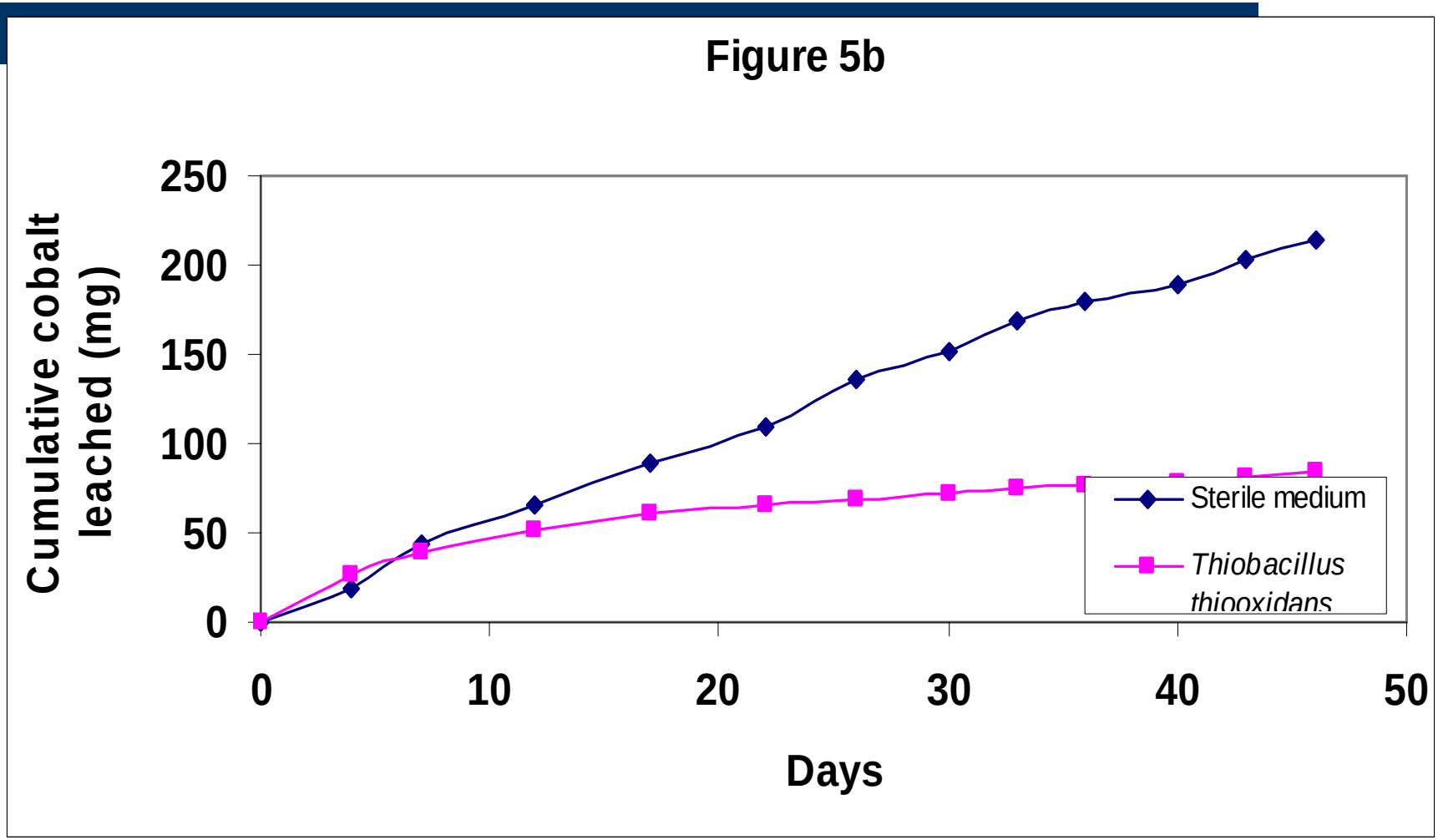


# Estimates of sulfate conc. in sterile medium and *T.t* broth showing evidence of substrate limitation in NRC Test.

| | Measured Sulfate Conc. (mg/L) | Max Derivable Sulfate Conc. (mg/L) | Available Sulfur in Test Cell (as mg/L sulfate) |
|---|---|---|---|
| Sterile Medium for Control | 574.0 | 4,310.0 | 3,736.0 |
| Fermenter broth for *T.t* Test | 4,355.0 | 4,310.0 | 0.0 |

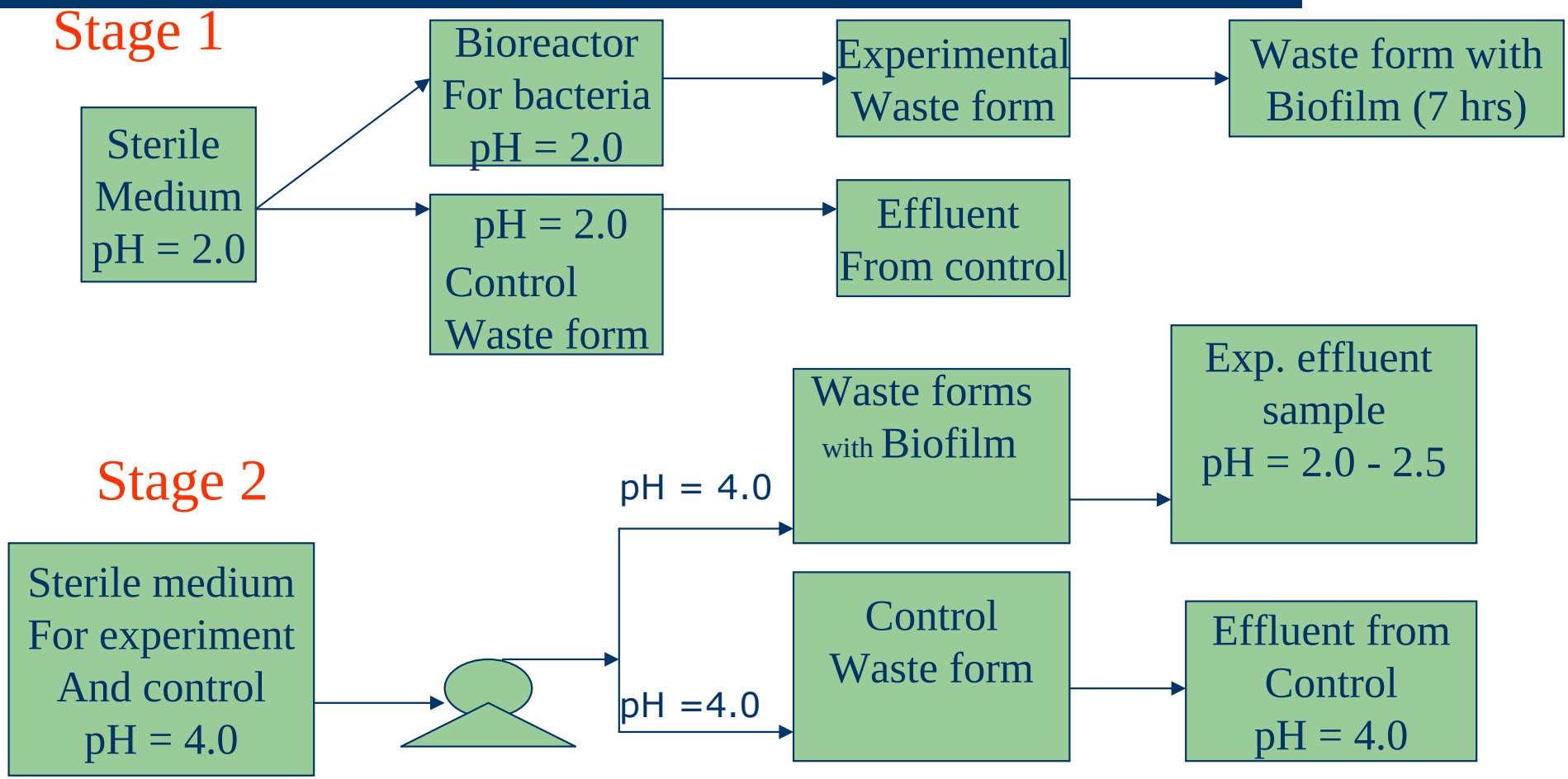
# Identified Technical Problems for NRC Test Protocol

- The waste form degradation observed during experimental MID test is due to initial high acidity (pH<2.0) in the pre-test microbial broth.
- The microbial broth used is substrate-limited, as available sulfur substrate is oxidized before contact with sample.
- The substrate limitation is due to the batch mode employed in the NRC test protocol.

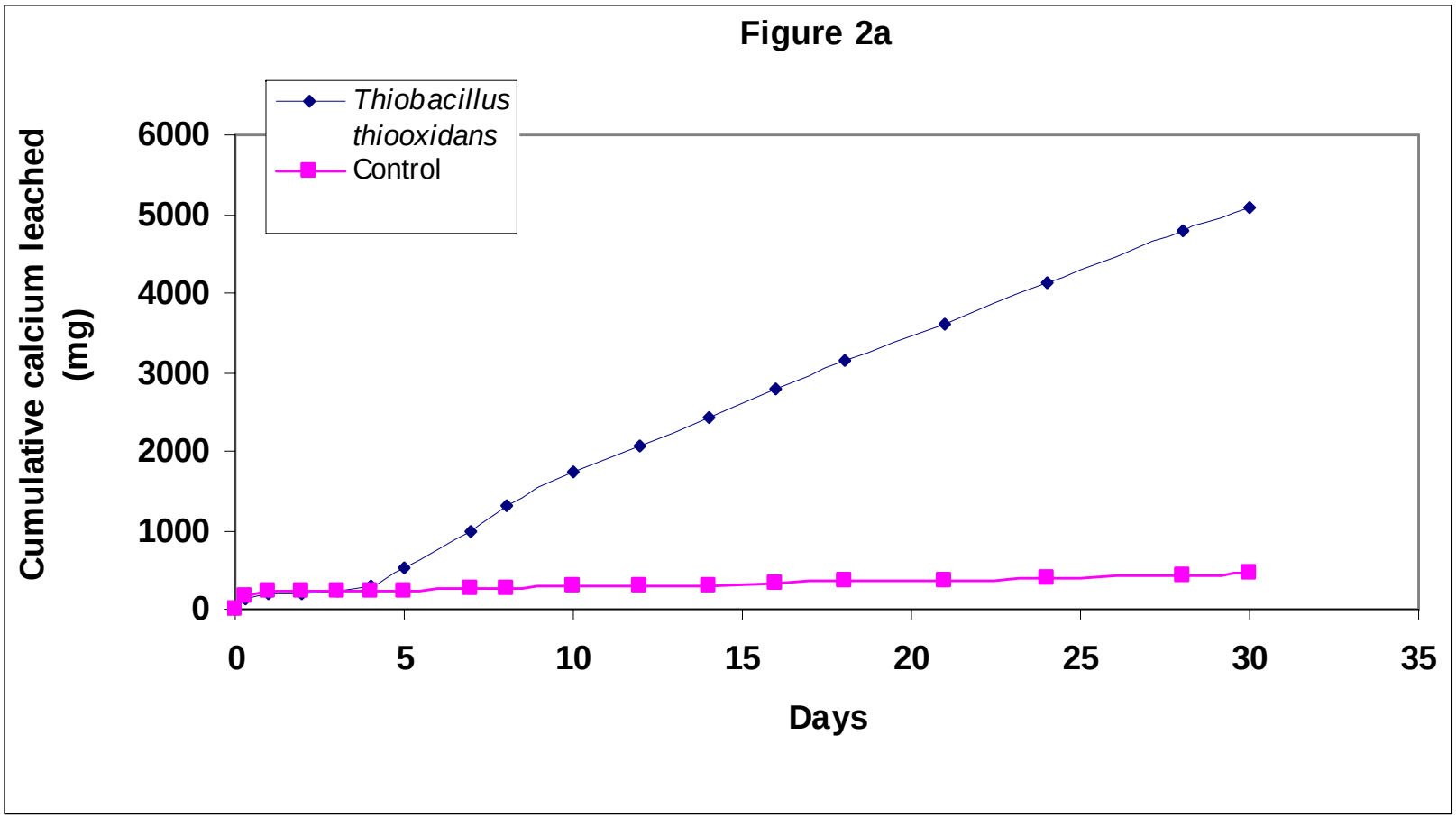
# Development of Alternative Protocol

- A two-stage Biofilm Formation test method was developed as follows:
  - Stage 1: Grow a microbial biofilm on the waste form surface before MID evaluation.
  - Stage 2: Take the sample with established biofilm, and conduct MID evaluation using a continuous flow of fresh medium (broth) at pH = 4.0

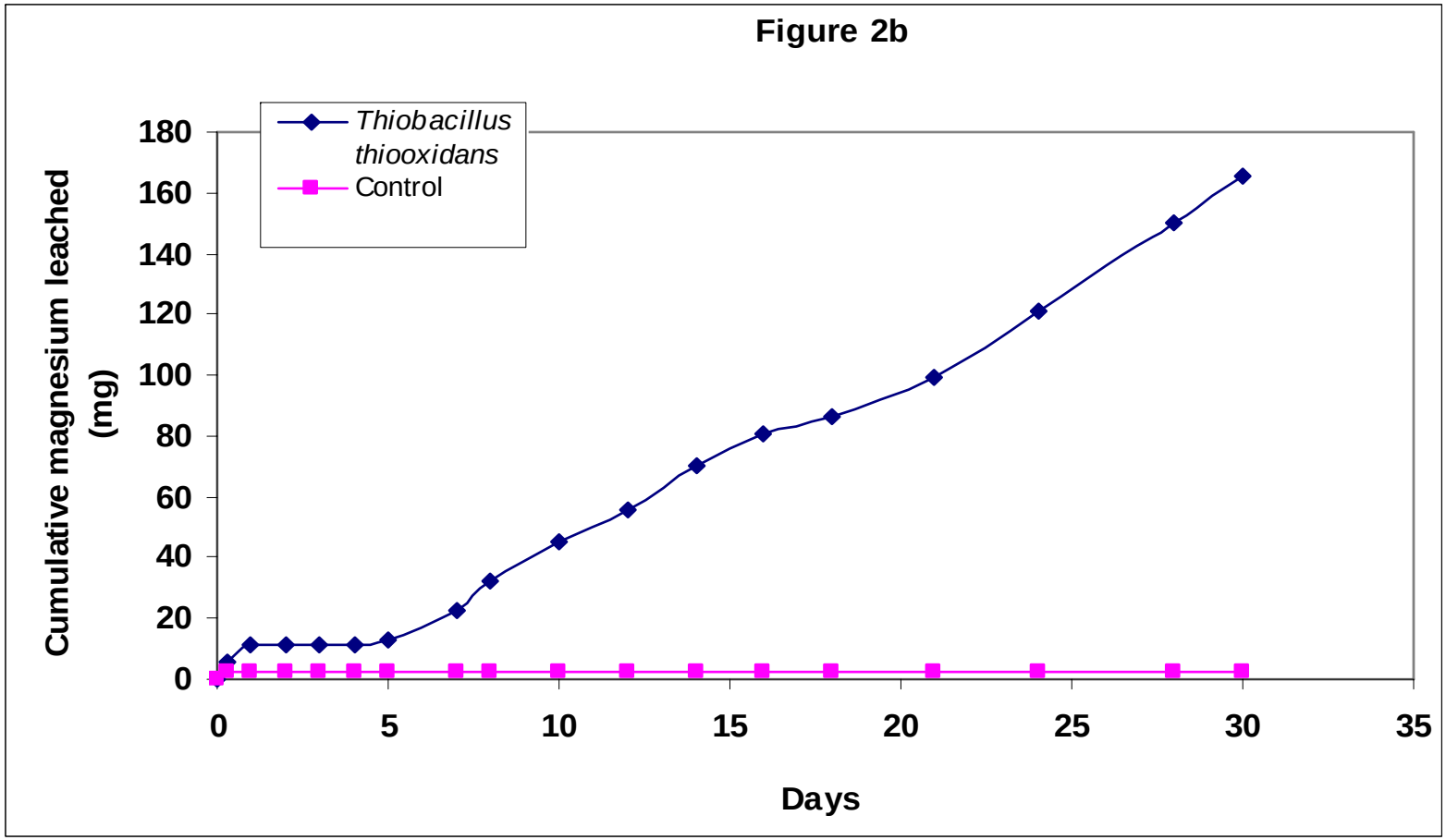
# Flow Diagram of the New Biofilm Protocol



# Calcium leached from cement waste forms using biofilm formation method (Biofilm Formation for 7 hours).



# Magnesium leached from cement waste forms using biofilm formation method (Biofilm Formation for 7 hours).



# Conclusions

Experimental evaluation of NRC's test protocol for MID of cement-solidified waste forms revealed several inadequacies including:

- The waste form degradation observed during the MID test is due mainly to the initial high acidity (pH<2.0) in the pre-test microbial broth, and not due to microbial induced degradation.

- The microbial broth used in the NRC method is substrate-limited, indicating a limited viability of the microorganisms during the test.

# Conclusions (contd.)

- The substrate limitation is due to the batch mode employed in the NRC test protocol.
- A new two-stage protocol, involving biofilm formation, was developed and tested to address the technical limitations of the NRC protocol.
- The new protocol clearly defines the role of microbes during MID degradation of cement-solidified waste forms.

# QUESTIONS !!!

- Contact information

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